1,107,206

PATENT SPECIFICATION

NO DRAWINGS

1,107,206

Inventor: DAVID POOLE KIDGER

Date of Application and filing Complete Specification: 1 Nov., 1965.

No. 46224/65.

Complete Specification Published: 27 March, 1968.

Index at acceptance:—C5 C(3A7, 9B9A, 9B9B, 9B9CX, 9B9D, 9C4, 9EX); A2 B15

Int. Cl.:—C 11 c 3/10

COMPLETE SPECIFICATION

Hard Butter and Chocolate Coating Composition containing same

We, NATIONAL BISCUIT COMPANY, a Corporation organized under the laws of the State of New Jersey, United States of America, of 425 Park Avenue, New York 22, State of New York, United States of America, do hereby declare the invention, for which we pray that a Patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to hard butter compound coatings.

Hard butter coating is the name used for edible products which exhibit good hardness at room temperature and melting characteristics suitable for handling and storage and which are still capable of retaining a pleasant appearance and good eating qualities in summer months.

Hard butters are triglycerides used in the manufacture of icings and the like, in the confectionery industry. They have the ability of taking bright colors, for instance yellow, pink and white. Hard butters, in combination with cocoa, sugar and an emulsifier, are also extensively used in chocolate-type coatings, that is, in the manufacture of chocolate coating materials for candies, ice cream bars, biscuits, cakes, cookies, chocolate bars, and icings.

Hard butter chocolate-type coatings are similar to pure chocolate coating, because they both contain a suspension of finely ground solids. In pure chocolate coatings, the solids are suspended in cocoa butter, while in hard butter coatings the solids are suspended in hard butters. The solids are a sweetening agent, for instance, sucrose, dextrose, saccharin compositions and malt powder, dry milk, buttermilk powder, salt, coloring agents and flavoring agents. An emulsifier is frequently added, for instance lecithin. Cocoa is used to impart the chocolate flavor.

Fats used in coating compositions, must meet certain standards. They must be free of the waxy tastes in the mouth, frequently associated with the fats used in this industry. The waxy taste is the result of hydrogenation widely practiced in the art, for the purpose of raising the melting range and obtaining products which are solid at room temperature. Although advantageous, where hydrogenation is complete or essentially complete, the products frequently are too hard, similar to waxes, do not melt sharply and give "waxy" feeling in the mouth, a feature which substantially diminishes their value in the food industry. Several studies have been made to remove the waxy feel. It has been found that, where the melting range is between 96°F. and 120°F., preferably between 96° and 114°F., a satisfactory fat is obtained, essentially free from the waxy taste. The hard butters which completely melt in this range, usually exhibit the property called a quick "get-a-way" and a pleasing "mouth feel". Thus this desirable property, which accounts for the freedom from the waxy taste, is mainly associated with the melting range of the fats.

Another requirement of fats used in coating compositions, is referred to as "fracture" or brittle" quality, or "snap", that is, they should remain essentially solid up to body temperature, 98.6°F., and then the entire mass should completely melt, in a short period of time. This requirement is usually difficult to meet because fats, in sharp contrast with other solids, are not definite single substances, but are mixtures of different triglycerides, and the melting point of a fat cannot be defined as it would be for a crystalline homogeneous substance, but it may have different meanings according to the method used for the determination.

The hard butters prepared from coconut oil and palm kernel oil by the process called "graining", still used in industry to a great extent, have the disadvantage of too low melting range, between 84° and 100°F. This process consists essentially of a fractional crystal-

[Pr

lization of the heated oil. The "grained" mixture is then pressed to squeeze the liquid from the crystallized material. Other processes have been directed to hydrogenation of the natural oil, for instance coconut, followed by a fractional distillation under high vacuum, to yield various fractions or units which meet the requirements for hard butters. The disadvantages inherent in the latter process, are mainly the losses due to distillation, decomposition, labor involved and high cost.

Another requirement is that the products be free from unpleasant odors, which are usually due to rancidity because of the presence of free fatty acids or oxidation.

Another requirement of the processes used in the manufacture of the fats for use as hard butter compound coatings is the control of the properties within narrow limits, namely, it is necessary to predict closely the melting range of the end products because the confectionery industry demands that the hard butters be very close in melting range to the specific temperature suitable for each individual operation. Essentially the hard butter compositions must have different specifications according to the season and the different types of confectionery. Reproducibility of results is particularly difficult in this art, because the fats used may vary in composition from year to year, and from one location to another. Bakery goods with "chewy" resistance, for instance crunchy nut rolls, need a higher-melting hard butter, but tender confections for instance marshmallow require a lower-melting fat. Essentially the hard butters used should be capable of standing firm at temperatures encountered in normal summer conditions without having some of their components bleed out or as it is usually referred to, "sweat". Similarly the finished food product should "stand up", that is, the coating should resist appreciable temperature changes, should not soften or stick to the center or other food product, so as to stain it, and it should not stick to the package.

Packing conditions must be considered because the melting temperature of the fat must be high enough to withstand the heat used in certain types of packing, which may be about 100°F. Baking conditions must also be considered and whether a fast or a slow cooling period is applied after baking. Obviously a short cooling tunnel requires a coating which sets more rapidly as compared to an apparatus where longer cooling time is provided. In general the coating should set or harden when it is enrobed or otherwise applied to a candy center or food product during the time allowed to pass through the cooling tunnel, so that when the piece emerges from the tunnel, it should be firm and ready for packing.

In the preparation of chocolate coating compositions, a serious disadvantage of all hard butters known in the art, is that they are not compatible with chocolate liquor, and incorporation of these hard butters together with chocolate liquor into coating compositions, changes the softening and melting characteristics of the hard butters. Even if the resulting coating compositions appear to be satisfactory for a few hours or days, fat bloom becomes evident on more prolonged storage. If chocolate liquor is incorporated into coating compositions to the extent of more than 4% together with the conventional hard butters, separation and fat blooming occur on standing. As a consequence, the manufacture in order to produce coatings which are stable to storage for at least two weeks, has kept the chocolate liquor content to less than 4% or have totally eliminated chocolate liquor and replaced it with cocoa.

The disadvantages inherent in the use of cocoa, essentially as the only chocolate ingredient, are manifest from a comparison of the compositions of cocoa and chocolate liquor. Since cocoa contains between 5 and 30% of cocoa butter, according to the method of manufacture, and chocolate liquor contains 50% of cocoa butter, the use of cocoa rather than chocolate liquor has given products with lower cocoa butter content and less rich flavor. The difference in composition between chocolate liquor and cocoa is due to the fact that essentially cocoa is manufactured from chocolate liquor by extraction of a substantial amount of the cocoa butter present. The residual press cake is then ground to give cocoa. In addition to the difference in cocoa butter content, the flavour and aroma deteriorate during the processing, particularly during the pressing operation, because of the heat development at the presses, which causes loss of the volatile flavouring components by evaporation.

It is manifest from the above that, if a hard butter could be manufactured compatible with chocolate liquor, the resulting coating compositions would offer equally rich flavour as compositions prepared from natural chocolate. The need in the art for a satisfactory hard butter capable of substituting cocoa butter and compatible with chocolate liquor, is so pressing that many attempts have been made to synthesize hard butter compatible with chocolate liquor for the purpose of improving the flavor of the finished products. Some synthetic hard butters are claimed to be compatible with chocolate liquor. Our studies of these synthetic products, however, indicate that they do not offer the solution to the problem. For instance, Feuge, Lovegren and Cosler in "Cocoa Butter-Like Fats from Domestic Oils", Journal of the American Oil Chemists Society, Vol. 35, p.194 (1958) have reported the results of their studies on the synthesis of cocoa butter substitutes by the esterification of mixtures of oleic, palmitic and stearic acids, or by the interesterification of their glycerides, followed by the fractional crystallization of the reaction products. Satisfactory results are reported with a fraction obtained from the interesterification

of 70 parts of completely hydrogenated cottonseed oil and 30 parts of olive oil, followed by fractional crystallization. The product thus obtained is incorporated into chocolate bar compositions, in the proportion of 21.9%, together with chocolate liquor in the proportion of 17.9%. The chocolate bars are reported to be stable when they are heated to 100°F. and then cooled back to room temperature.

In spite of the successful results reported, the hard butters prepared as described in the above-cited publication, are not suitable for large-scale commercial application, and the coatings containing these hard butters and chocolate liquor, to the extent of 17.9% of the latter, as described, are not stable on storage, and after standing at room temperature for merely two weeks, fat bloom occurs.

As late as May 1964, in "Marketing Potentials for Modified Edible Fats and Oils", Marketing Research Reports No. 659, U.S. Department of Agriculture. Economic Research Service, Marketing Economics Division, p 17 (May 1964). the shortcomings of cocoa butter substitutes are discussed, namely incompatibility with chocolate liquor, improper gloss, rancidity, and no ready solution for the problem is foreseen. It is clear from this publication, that no substantial progress has been made towards the preparation of hard butter compositions compatible with chocolate liquor, prior to this instant invention.

An object of the present invention is to provide hard butter compositions which are solid at room temperature, but which melt sharply as soon as the body temperature is reached.

Still another object is to provide improved hard butters which are completely melted in the range of 96° to 115°F., and which are essentially free of the waxy mouth feel.

A further object is to provide compositions suitable as hard butter coatings, with superior gloss and a high degree of palatability.

It is a further object of the present invention to provide a process which utilizes readily available low-cost raw materials, and substantially all of the raw materials, converting them into hard butters suitable for incorporation into the finished products.

Another object of this invention is to provide a simple and economical process which permits the preparation of hard butters, compatible with chocolate liquor, with preselected melting characteristics according to the season and climate, and with a high degree of reproducibility.

Another object of this instant invention is to prepare hard butters which are compatible with chocolate liquor, so that chocolate coating compositions may be prepared containing chocolate liquor in amount up to 45% of the finished coating composition.

Another object of this invention is to utilize marine oils, namely herring oil, menhaden oil, sardine oil, whale oil, and mixtures of the several marine oils.

One of the starting materials in practicing the invention, which will be called component A, is a high molecular weight fully hydrogenated fat. It has been found that the inexpensive animal fats, lard and tallow are very satisfactory. Also marine oils, such as herring oil, menhaden oil, sardine oil and whale oil may be used. The unpleasant odors present in marine oils, due to lower boiling components, are easily and completely removable by distillation and do not interfere with the finished products. Also vegetable oils may be used such as soybean oil, cottonseed, sesame oil, sunflower oil, safflower oil, peanut oil, palm oil, or corn oil, but they are usually more expensive. The fats from the different animal and vegetable and marine sources may also be combined according to different proportions.

Oleic acid is a substantial component in all the fats used to prepare component A. Oleic acid is present in amount varying between 41 and 51% in lard, 39 to 50% in beef tallow, and 36 to 47% in mutton tallow. It is also present in considerable amount in the marine oils, and in the vegetable oils used in accordance with this invention. Essentially the amount of oleic acid varies between a lower limit of about 12% in menhaden, 15% in safflower and 17% in soybean to a maximum of 71% in peanut oil. Thus one of the essential components in this fraction is a C_{18} acid with just one site of unsaturation. Another component is palmitic acid, that is a C_{16} acid, which is present up to 47% in palm oil, but which may be as low as 3% in sunflower and safflower oil. By varying the proportions of the fats it is possible to have the desired proportion of palmitic acid, up to 47% of the total of component A. It is another essential characteristic of the invention that all the facts utilized individually or in mixtures to prepare component A be free from lauric acid.

One of the fats listed above or a mixture of them is hydrogenated. Hydrogenation may be conducted according to conventional processes, but catalytic hydrogenation with hydrogen under pressure and a catalyst, for instance reduced Nickel on Kieselguhr, has proved very satisfactory. The preferred conditions are 2 to 45 pounds of hydrogen pressure at a temperature of 100° to 225°C. Hydrogenation is allowed to proceed until the desired refractive index and iodine value are obtained corresponding to essentially complete hydrogenation. The iodine value of the reduced composition should never be above 5 and is usually below 5. According to the preferred embodiment of this invention, the iodine value of component A is not above 3 and essentially all the oleic acid is reduced to stearic acid.

This component A which confers hardness and high melting characteristics to the resulting product is called "all-hydrogenated", it being

understood that small amounts of unsaturation may still be present.

The second component used in practicing the invention, called component B, is a lauric acid-containing vegetable oil. Typical instances of oils containing lauric acid are palm kernel oil and coconut oil. Although palm kernel and coconut oil are shown in the examples, babassu oil, which contains between 44 and 56% of lauric acid, may be used. In accordance with the invention, coconut oil and palm kernel oil are subjected to partial reduction. The extent of reduction is carefully controlled according to the instant invention to provide products which after combination with component A and furher processing as described herein, are free from "waxy feel". The extent of hydrogenation should correspond to about one-half of the unsaturation originally present. For practical purposes, the hydrogenation of coconut oil, which has an iodine value of 10 is allowed to proceed until the iodine value of the product is about 5, corresponding to a refractive index at 60°C. of 25, and palm kernel oil is hydrogenated until the iodine value is 12, corresponding to a refractive index of 25.8 at 60°C.

An increase in hydrogenation up to the iodine value of 4 for coconut oil and 10 for palm kernel oil is possible without too unfavourably affecting the properties of the final products but further hydrogenation would give inferior products.

The conventional processes may be used for the incomplete hydrogenation of coconut and palm kernel oil. Good results have been obtained with reduced nickel on kieselguhr at a temperature of 150° to 225°C. and a pressure of 2 to 45 pounds of hydrogen. This hydrogenation step is usually complete for a batch of two kilograms of the coconut oil after one and half minutes but it requires 20 minutes for palm kernel oil. The product from the incomplete hydrogenation of palm kernel and coconut oil is called component B, it being understood that a preselected mixture in varying proportions of the incompletely hydrogenated palm kernel and coconut oil may also be used. It has now been found that mixtures comprising the two components A and B may be blended in different selected proportions, and then subjected to interesterification. The melting characteristics and physical qualities of the end products, by a selection of the constituents of component A and B may be controlled within a narrow range as it will be described below.

The mixtures of component A and B before interesterification still exhibit the *beta* structure, but the products after interesterification in accordance with the invention exhibit the *beta prime* structure.

It has been found that inverting the products, that is using as component A, an oil which does not contain a substantial amount of unsaturated components and which contains a substantial amount of lauric acid, for instance babassu oil, together with, for instance lard as component B which contains a substantial amount of oleic acid, is not satisfactory. It is probable that the greater amount of oleic acid and other unsaturates still present under these conditions due to the incomplete hydrogenation of lard if it were used to prepare component B, is responsible for the poor results but the scope of the invention may not be limited by any explanation of speculative nature.

The relative proportions of the all-hydrogenated oil and the partially hydrogenated oil may vary widely, but in all cases the all-hydrogenated component is in a proportion not greater than 50%, and not less than 10%. The interesterification reaction is also called in the art "rearrangement". The preferred catalysts are basic anhydrous substances, such as sodium, potassium, alkali metal alkoxides having up to 4 carbon atoms, alkali metal hydrides as sodium hydride, and alkali earth metal hydride, as for instance calcium hydride. Aluminum alkoxides and lithium aluminum hydride may also be used. The catalysts are effective at temperature below 150°C., where the components A and B are present in a single liquid phase. The amount of catalyst should be kept at a minimum, and in order to avoid saponification of the glycerides, should not be in excess of 1%, and preferably 0.2% by weight. Since the catalyst is easily destroyed by moisture, carbon dioxide and air, it is advantageous to dry the mixture thoroughly before the interesterification reaction. Heating under *vacuo* to remove moisture is satisfactory. The reaction is conveniently carried out in an atmosphere of nitrogen or hydrogen at a temperature of about 140°C. The effectiveness of the catalyst and the completeness of the reaction may be easily followed by the color change, the mixture darkening and acquiring a reddish color. The rearrangement usually occurs very rapidly but in order to ensure complete rearrangement, heating is continued for about one-half hour. The mass then is cooled to about 90°C. and the excess catalyst is destroyed with water or dilute acid.

The physical properties of the blend are different from those of the unrearranged mixture of component A and B. Some of the physical properties which are altered by catalytic rearrangement are melting characteristics, melting range, congeal point, plasticity, crystallization characteristics and eating characteristics. It is very likely that the improvement in the properties which characterize a good hard butter is related to the conversion of the *beta* to the *beta prime* structure after interesterification as mentioned above. The improvement in melting characteristics and other physical properties are also due to the greater homogeneity of the final products. Interesterification essentially converts the mixture of the two

components A and B into a new product, which, although still a mixture of triglycerides is the result of chemical reaction, namely an exchange of acyl radicals between A and B, the achievement of "random" distribution, as defined in Gilman "Advanced Treatise of Organic Chemistry", Vol. III (1853), pp. 186—190.

It has been found advantageous to determine the Solid Fat Index for different percentage compositions of component A and B against the temperature in Fahrenheit. The determination is made from the specific volumes at various temperatures according to the method CD—10—61, described in Official and Tentative Methods of the American Oil Chemists Society (1961). The different values obtained for several compositions 10 to 40% of component A and 90 to 60% of B with increase in temperatures are shown in the tables. The Solid Fat Index was plotted as the ordinate with the temperature on the abscissa, for several of the compositions prepared according to this invention. It was found that the curves are quite flat in the lower temperature range up to 70°F., retain a sufficiently high Solid Fat Index at room temperature, for compositions of A at least 10% and B not over 90%. Then the curves become less flat in the region between 70 and 80°F., and still less flat above 80°F., indicating that melting occurs rapidly in this region.

Examination of the plots also showed that the results obtained according to this invention, with the less expensive animal fats, namely lard and tallow are just as good as with the vegetable oils, in the range 10 to 40% of component A to B. The results below also show very satisfactory results with a marine oil namely menhaden.

As it has been mentioned it is possible to select the proper constituents of component A and B, as well as the respective proportions of A and B for each desired hard butter. This may be accomplished simply by application of the data in the tables, the respective plots and in some cases interpolation.

For the purpose of better illustrating the invention the following examples are described in detail.

Example

Two kilograms of lard was fully hydrogenated using 0.2% reduced nickel on kieselguhr at 30 p.s.i. of hydrogen and at a temperature of 200°C. The resulting fully hydrogenated lard was subjected to flaking. The refractive index was 31.3, corresponding to an iodine value of 3. 2Kg. of coconut oil was hydrogenated under the same experimental conditions, but the reaction was interrupted when the refractive index of a sample measured at 60°C. was 25. This corresponds to iodine value of 5. Seven hundred grams of the incompletely hydrogenated coconut oil were mixed with 300 grams of the flaked lard prepared as described above and heated about one-half hour above 100°C. in an atmosphere of nitrogen to remove moisture. This corresponds to 30% of component A and 70% of component B. Then a catalytic amount of sodium methoxide, about 0.2% was added. The mixture was kept at a temperature of 120°C. Interesterification rapidly took place as evidenced by the development of a red color. The content of the flask was cooled to 90°C., water in amount about 25% in excess over the amount of catalyst added was used to destroy the catalyst. Solid by-products "foots", that is soaps due to hydrolysis of the fats were separated from the oil by filtration. The resulting product was deodorized by high *vacuo* steam distillation. The product gave a very satisfactory hard butter, because it was stable and bleeding out of individual compounds at a temperature of 80°F. did not occur. The gloss was good with no change on storage.

Several compositions were prepared in ratios of lard flakes to partially hydrogenated coconut varying between 10 and 40%. The products were very satisfactory hard butters in every respect state, color, viscosity, set point. The table below gives the values of the Solid Fat Index at different temperatures.

TABLE 1

Solid Fat Index of Lard Flakes with Partially Hydrogenated Coconut Oil

T°F.	% Composition of Lard Flakes			
	10%	20%	30%	40%
50°	51.4	54.8	61.0	64.4
70°	31.1	37.9	48.5	54.9
80°	14.8	26.4	39.3	47.4
92°	0.2	5.4	16.6	26.5
100°	0.0	0.2	3.0	11.7
104°	0.0	0.0	0.0	5.7

The Solid Fat Index was plotted as the ordinate and the temperature as the abscissa to show the variations in the region between 50° and 104°F. The composition 10% of A to 90% of B in the region between 50° and 70°F. showed a decrease in Solid Fat Index of about 1, per degree of temperature rise. In the same range the composition 40 to 60% showed a decrease of 0.47 per degree indicating that when the hydrogenated lard is kept at the lowest proportion, the composition undergoes a more gradual softening while the 40 to 60% composition shows a superior "stand up" quality in this region. In the region between 92° and 100°F. the composition 40 to 60% showed a decrease of 1.8 units per degree, while with the composition in which hydrogenated lard is kept at the lowest value the material has practically already totally melted.

The X-ray diffractometer marketed by the Norelco Co., was used for the study of the composition of the product before and after interesterification. The *beta* structure was prevalent before interesterification as shown by the short spacings of 3.68 (Medium), 3.86 (Medium), 4.59 (Strong) and 5.3 (Weak), in agreement with the data reported for the beta form, for instance in Mehlenbacher "The Analysis of Fats and Oils", The Gerrard Press, (1960) p. 410. After interesterification, the short spacings were 4.18 (Strong) and 3.78 (Medium), as reported for the *beta prime* by the same author.

EXAMPLE 2

Flaked tallow was prepared from tallow by hydrogenation and flaking essentially in the same manner as described above for lard. Palm kernel oil was hydrogenated in the same manner as coconut oil but hydrogenation was stopped when the refractive index was 25.5 to 25.7 at 60°C. Four hundred grams of flaked tallow and 600 grams of incompletely hydrogenated palm kernel oil were subjected to interesterification as in Example 1 and then deodorized. The product was satisfactory as a hard butter in chocolate type coatings, in taste, appearance, freedom from odor. The Solid Fat Index for this 40 to 60 per cent composition is given below, as well as for other compositions in which tallow is the range of 10 to 40% of the total.

TABLE 2

Solid Fat Index of Compositions of Hydrogenated Tallow with Partially Hydrogenated Palm Kernel Oil

	% Composition of Hydrogenated Tallow			
T°F.	10%	20%	30%	40%
50°	61.7	62.5	70.3	68.9
70°	46.3	51.4	62.8	63.4
80°	33.7	41.9	55.4	57.4
92°	6.3	14.5	27.8	35.1
100°	0.0	0.3	12.2	15.4
104°	0.0	0.3	3.0	7.6

The Solid Fat Index was plotted as hereinbefore described to show the rate of decrease of the Solid Fat Index in the region between 50° and 104°F. for the compositions of the invention. In the region up to 70°F. the decrease is about 0.77 per each degree of temperature rise, for a composition of 10% of hydrogenated tallow to 90% of partially hydrogenated palm kernel oil. In this low temperature region the composition 40 to 60% shows a Solid Fat Index decrease of only 0.27 per degree. In the region between 92 and 100°F. the composition 10 to 90% shows a decrease of only 0.78 per degree rise of temperature but the composition 40 to 60% shows a decrease of 2.4 per each degree of temperature rise. Thus it is obvious that the composition containing a greater amount of hydrogenated tallow retains its solid character essentially up to 80°F. and then melts sharply.

X-ray studies, with the same instrument as described above showed that interesterification totally eliminates the *beta* structure and converts the products into the *beta prime* structure. Similar results were obtained with other fats as component A and B and for the puropse of better illustrating the invention, a few more examples are given. The data for the Solid Fat Index at different proportions of soybean flakes with partially hydrogenated coconut oil are given below.

TABLE 3

	% Composition of Soybean Flakes			
T°F.	10%	20%	30%	40%
50°	50.3	55.5	60.0	59.9
70°	29.7	38.3	47.3	47.9
80°	14.6	26.8	37.9	40.6
92°	0.2	5.2	14.8	21.5
100°	0.0	0.0	3.2	10.1
104°	0.0	0.0	0.4	5.6

The results with tallow and coconut oil are shown below.

TABLE 4

T°F.	% Composition of Hydrogenated Tallow 10%	20%	30%	40%
50°	53.4	57.0	59.2	64.7
70°	32.9	39.9	46.1	53.6
80°	16.5	27.8	36.5	46.1
92°	0.0	5.0	13.4	27.6
100°	0.0	0.0	1.7	16.5
104°	0.0	0.0	0.0	11.4

The finding that the proportion of component A must be between 10 and 50% of the composition is strikingly shown by the data shown below:

TABLE 5

T°F. +	5% Hydrogenated Lard 95% Partially Hydrogenated Coconut Oil	60% Hydrogenated Lard 40% Partially Hydrogenated Coconut Oil
50	50.4	71.7
70	30.0	65.7
80	9.8	61.7
92	0.0	48.3
100	0.0	33.1
104	0.0	25.2

It is clear from the data, that with fully hydrogenated lard and partially hydrogenated coconut oil, at a proportion 5% of the former and 95% of the latter, the material is all liquid at 92°F. On the other hand the composition 60% lard flakes to 40% coconut oil is still to a great extent not melted at 104°F. and would be unsuitable as a hard butter because it would leave a "waxy feel".

Our experiments with marine oils have shown that they may be satisfactorily used as component A, after full hydrogenation, with component B. The result with menhaden flakes, that is fully hydrogenated, together with palm kernel oil, partially hydrogenated are shown below:

TABLE 6

T°F.	% Composition of Menhaden Flakes 10%	20%	30%	40%
50	63.4	62.3	65.2	68.0
70	53.9	49.7	55.4	60.1
80	39.4	37.2	45.2	53.3
92	9.6	10.6	21.3	32.1
100	0.0	0.0	3.8	13.5
104	0.0	0.0	0.2	7.2

Other compositions tested in the same proportions indicated in Table 6 where:

Cottonseed flakes either with palm kernel oil, of refractive index 25.5 or coconut oil of refractive index 25, also sunflower flakes, peanut flakes, safflower flakes with coconut oil of refractive index 25. The results were satisfactory in every respect. In each instance the *beta* configuration was converted into the *beta prime* configuration.

Excellent results have been obtained by incorporating the hard butters in chocolate-type coatings, icings, and confectioners coatings. The ranges of typical coating formulations used in chocolate-type coatings are shown below, where the figures are expressed in per cent.

TABLE 7

Chocolate Coating Formulations

	Dark Compound	Light Compound
Hard Butter	31.5	31.5
Cocoa	18—17	8.0
Skim Milk Powder	6—8	6—8
Sugar (4x or slightly coarser in grind)	43—45	53
Salt	0.20	0.2—0.3
Vanillin	0.10	0.10
Lecithin	0.35	0.35

The hard butter in the formula may be any of the compositions according to this invention, that is they are made from a component A which may be of animal or vegetable origin.

All the ingredients are measured and combined with the exception of about one-half of lecithin and a small portion, about 2 to 4% of the hard butter. After blending, the temperature of the mix is 120° to 145°F. The blend is refined to reduce the particle size to a range between 25 and 40 microns. The coating is placed in storage tanks, at temperature of 135° to 145°F. for about 24 hours, during which time it is stirred in order to lower and stabilize the viscosity. The residual portion of 2 to 4% hard butter and lecithin are then added for the purpose of further lowering the viscosity. The coating is then tampered and molded into blocks, or kept in the melted state. It may be shipped either in the solid or melted form.

It is stable over a period of at least one year and coatings prepared from the stored material are not inferior to coatings prepared immediately.

WHITE COATING

A white coating was prepared by blending 33 lbs. of a hard butter prepared in accordance with the invention, 18 lbs. of milk solid powder, 49 lbs. of fine sugar. 3 oz. of salt, ½ lb. of vanilla and 2.5 oz. of lecithin. The product was very satisfactory in stability, taste and was free from the waxy mouth feel.

In a particular aspect of the present invention it has been found that when marine oils are used as component A, the resulting hard butters, after combination with conventional coating ingredients and incorporation into coating compositions, impart unusual shine and gloss to the compositions. Further it has been found, surprisingly, that the hard butter compositions prepared from marine oils as component A are compatible with chocolate liquor and that chocolate liquor may be incorporated into the coating compositions to substitute in part and even to eliminate totally the use of cocoa. Thus, while with the conventional hard butters, the amount of chocolate liquor could never exceed 4% of the total coating compositions, and the use of mixtures of chocolate liquor and cocoa containing a substantial amount of cocoa was necessary, as it has been mentioned above, according to this instant invention, the amount of cocoa may be substantially decreased and even totally eliminated.

It is manifest from the above, that this aspect of the invention represents a revolutionary advance in the confectionery industry, because of the manifest superiority of chocolate liquor over cocoa, as the chocolate-ingredient. As compared with the flavour of cocoa-containing coating compositions, the compositions prepared with chocolate liquor offer a rich, full, natural flavor, comparable with natural chocolate. Thus the coating compositions prepared in accordance with the process described herein, exhibit palatability and flavor, superior to coating compositions prepared from conventional hard butters and cocoa. Further, because of the high cocoa butter content of chocolate liquor, in the range of 50%, it is possible to decrease the proportion of hard butter in the coating compositions, and still retain the softness of the coating.

All the marine oils, menhaden, herring oil, sardine, whale oil, or their mixtures, may be used in accordance with this aspect of the invention. The resulting compositions exhibit good compatibility with chocolate liquor and superior shine.

According to the preferred embodiment of this aspect of the invention, herring oil, is used. In its broad concept, herring oil is fully hydrogenated, then combined with palm kernel oil, in the ratio of 10 to 50% of hydrogenated herring oil to palm kernel oil in amount between 90 and 50% of the latter. The mixtures are then interesterified according to conventional methods, in the presence preferably of sodium methoxide, as a catalyst, and the resulting products subjected to high vacum steam distillation, to remove low boiling decomposition products. The resulting hard butters are then combined with the ingredients used in coating compositions, in preselected proportions.

It seems reasonable to assume that the superior gloss and the high degree of compatibility of the hard butters prepared as described herein, with chocolate liquor, are the result of the high proportion of high-molecular-weight unsaturated fatty acids present in marine oils. The composition of herring oil, which gives the best coating compositions, is a typical illustration. This oil contains about 24% of fatty acids containing 22 carbon atoms, for instance docosenoic acid, and about 25% fatty acids containing 20 carbon atoms, for instance eiocosenoic acid. The proportion of C_{20} unsaturated fatty acids is high in all marine oils, because it is 18—26% in sardine oil, depending on the origin, whether it is the California sardine oil or Japanese sardine oil, 19% in menhaden oil, and 12% in whale oil. The fraction of the unsaturated acids containing 22 carbon atoms, is high also in the other marine oils, because it is 14—19% in the sardine oils, 11.7% in menhaden and 7.% in whale oil.

For the purpose of better illustrating this aspect of the invention, the following example is given.

Example 3

Two kilograms of herring oil were fully hydrogenated using 0.2% reduced nickel on Kieselguhr at 30 p.s.i. of hydrogen and at a temperature of 200°C., and then flaked.

Two kilograms of palm kernel oil were hydrogenated until the refractive index was 25.5 to 25.7 at 60°C. Eight hundred grams of the incompletely hydrogenated palm kernel oil, were mixed with 200 grams of the flaked herring oil prepared as described above, and heated about one-half hour at 120°C. in an atmosphere of nitrogen to completely remove the moisture. The mixture contained 20% of component A and 80% of component B. Then a catalytic amount of sodium methoxide, about 0.2%, was added, and the mixture was kept at a temperature of 120°C. about one-half hour. Interesterification occurred rapidly, as evidenced by the development of a red color. The content of the flask was cooled to 90°C. and water, in amount about 25% in excess over the amount of catalyst added, was used to destroy the catalyst. Solid by-products "foots", that is soaps due to the hydrolysis of the fats were separated from the oil by filtration. The resulting product was deodorized by high vacuum steam distillation.

Several compositions were similarly prepared in proportion of between 10 and 50% of herring flakes and between 90 and 50% of partially hydrogenated palm kernel oil.

The solid Fat Index was determined for each composition at different temperatures, in the range between 50° and 104°F. The determination of the Solid Fat Index was made from the specific volumes at various temperatures according to the method CD—10—61, described in Official and Tentative Methods of the American Oil Chemists Society (1961). The different values obtained for several compositions comprising between 10 and 50% of component A, and between 90 and 50% of B with temperature rise from 50 to 104°F., are shown in the table below.

TABLE 8

Solid Fat Index of Herring Flakes with Partially Hydrogenated Palm Kernel Oil

T°F.	10%	20%	30%	40%	50%
50	61.0	62.5	64.1	66.2	68.2
70	45.6	50.0	53.3	57.1	60.6
80	29.4	37.2	44.0	49.3	54.8
92	1.4	8.1	16.0	28.2	36.3
100	0.0	0.0	2.1	10.8	18.5
104	0.0	0.0	0.2	5.6	11.4

It is manifest from the Table above, that, in the range between 50° and 92°F., the Solid Fat Index of the compositions containing only 10% of herring flakes, decreases at the rate of about 1.4 units per degree, while the compositions show superior "stand up" quality, in the same temperature range, when the proportion of fully hydrogenated herring oil is 40% and 50%. With the higher proportion of herring flakes, 40%, the decrease of Solid Fat Index in the same temperature range is lower, only 0.9 units per degree Fahrenheit, and with the proportion of 50% of herring flakes, the decrease in Solid Fat Index per degree Fahrenheit in the same temperature range, is only 0.75 unit.

At a temperature of 100°F., the Solid Fat Index is zero when the proportion of hydrogenated herring oil is between 10 and 20%. When the proportion of fully hydrogenated herring oil is 30%, the Solid Fat Index at 100°F., is close to zero. With compositions containing 40% of herring oil, the Solid Fat Index is 10.8 at 100°F., thus making the composition in this range more suitable for hot weather coating.

Similar results were obtained from a blend of herring flakes and partially hydrogenated coconut oil, that is coconut oil, hydrogenated until the refractive index is 25 to 60°C., and the iodine value is 5. The two components were blended in the ratio of 10% to 50% herring flakes and 90 to 50% of the partially hydrogenated coconut oil, and then interesterified. The different values of the Solid Fat Index at different temperatures, for different compositions, are shown in Table 9

TABLE 9

Solid Fat Index of Herring Flakes with Partially Hydrogenated Coconut Oil

T°F.	10%	20%	30%	40%	50%
50	56.6	57.40	60.2	66.5	—
70	38.5	42.8	49.1	58.3	63.2
80	21.7	30.5	39.9	51.3	58.3
92	0.4	6.2	16.9	31.2	42.5
100	0.0	0.0	3.0	13.7	25.5
104	0.0	0.0	0.7	8.2	18.5

It is manifest from the results of Table 9 that at temperature of 100°F., the Solid Fat Index is zero for the compositions containing 10% and 20% herring flakes and only 3% for compositions containing 30% herring flakes.

The results with menhaden flakes and partially hydrogenated coconut oil, were also satisfactory. The values of the Solid Fat Index at different temperatures and for different compositions are shown in Table 10.

TABLE 10

Solid Fat Index of Menhaden Flakes and Partially Hydrogenated Coconut Oil

T°F.	10%	20%	30%	40%	50%
50	55.8	58.2	61.1	64.5	65.3
70	38.3	43.0	48.8	56.1	59.5
80	18.7	27.5	35.8	50.3	53.3
92	0.4	4.8	12.4	32.0	34.4
100	0.1	0.1	1.1	15.9	17.4
104	0.0	0.0	0.2	9.6	10.6

The table above shows that at temperature of 100°F., the Solid Fat Index is essentially zero for the compositions containing 10 and 20% menhaden flakes, while the compositions containing 40 and 50% of herring flakes show superior "stand-up quality" in the temperature range between 50 and 92°F.

In the formulations shown in Table 7, cocoa is the chocolate ingredient, and chocolate liquor may be incorporated in the coating compositions, only to the extent of 4%. If the proportion of the chocolate liquor is increased to 5%, separation and blooming occurs. On the other hand, where the hard butters prepared from marine oils are used in the same formulations of Table 7, chocolate liquor may be incorporated safely, without blooming, and the amount of cocoa may be decreased, with consequent improvement in flavor.

The results with two compositions, compositions 1) from a hard butter prepared from lard, tallow or soybean flakes and composition 2) from a hard butter prepared from herring flakes, and partially hydrogenated palm kernel oil in the ratio of 30 to 70, are shown below in Table 11.

TABLE 11

Ingredients	Amount of Ingredient %	Results with Composition 1	Results with Composition 2
hard butter	30	Dull; blooming began after 2 weeks' storage	Very good shine, No blooming after 6 months' storage
cocoa	15—18		
chocolate liquor	5		
sugar	38—40		
skim milk solid	5—6		
vanillin	0.08—0.1		
salt	0.15—0.2		
lecithin	0.3—0.4		

It is manifest from the results above that chocolate liquor may be used in combination with the hard butters prepared from herring oil, but it may not be incorporated into coating compositions containing the other hard butters, not even in the amount of 5%. On the other hand, Composition 2, above, showed excellent shine and stability even after 6 months' storage.

Several variations of the formulations shown in Table 11 above, were made, increasing progressively the amount of chocolate liquor and decreasing the amount of cocoa. Obviously, with increasing concentration of chocolate liquor, it becomes necessary to decrease the overall amount of hard butter because of the high cocoa butter content of chocolate liquor. The stability and gloss were very satisfactory, even when the percentage of chocolate liquor was increased to 45%.

When the proportion of chocolate liquor is increased to 10%, the amount of hard butter prepared from 30% herring flakes and 70% partially hydrogenated palm kernel oil is decreased to 29% and the amount of cocoa is also decreased to 14%. The other ingredients in the formulation, sugar, skim milk, vanillin, salt, lecithin are kept essentially constant, that is, between 5 and 6% of milk solid, between 38 and 40% of sugar, between 0.3 and 0.4% of lecithin, vanillin in amount up to 0.1%, and salt in amount of 0.1 to 0.2%. After six months' storage, the coating composition containing 10% chocolate liquor, was stable, exhibited excellent shine, and was free from blooming.

When the chocolate liquor is increased to 15%, the hard butter prepared from 30% herring flakes and 70% partially hydrogenated palm kernel oil is decreased to 28%, the cocoa is decreased to 11%, maintaining the other ingredients essentially constant, that is between 5 and 6% of milk solid, between 37 and 38% of sugar, between 0.08 and 0.1% of vanillin, between 0.1 and 0.2% of salt, and lecithin, in amount between 0.3 and 0.4%. After four month's storage, the composition exhibited excellent shine and was free from blooming. With still increasing proportion of chocolate liquor, that is 20%, the amount of hard butter prepared from 30% herring flakes and 70% partially hydrogenated palm kernel oil, is decreased to 25%, the cocoa is decreased to 8%, the other ingredients being kept essentially constant, that is, sugar at 37—38%, milk solid between 5 and 6%, vanillin in amount up to 0.1%, salt in amount between 0.1 and 0.2%, and lecithin between 0.3 and 0.4%.

With increasing proportion of chocolate liquor, namely 25%, the amount of cocoa is decreased to 7%, and the amount of the hard butter prepared from 30% herring flakes and 70% partially hydrogenated palm kernel oil, is decreased to 20%. The other ingredients are kept essentially constant, that is the amount of sugar is between 37 and 38%, milk solid between 5 and 6%, the amount of vanillin is between 0.08 and 0.1%, salt between 0.1 and 0.2%. After four months' storage, the coating composition exhibited very good shine and was free from blooming.

When the chocolate liquor is increased to 35%, the amount of the hard butter of the invention, containing 30% herring flakes and 70% partially hydrogenated palm kernel oil, is decreased to 14%, and the amount of cocoa is only 1—2%. The proportion of sugar is still between 37 and 38%, milk solid between 5 and 6%, vanillin between 0.08 and 0.1%, salt between 0.1 and 0.2%, and lecithin between 0.3 and 0.4%. This coating composition is stable and free from blooming for a period of at least two months.

With 45% chocolate liquor, the cocoa is totally eliminated and the proportion of the hard butter of the invention, prepared from 30% herring flakes and 70% partially hydrogenated palm kernel oil, is decreastd to 10%. The other ingredients are essentially the same as in the composition above. This composition is stable for about a month, and blooming does not occur until after a one-month period has elapsed. Thus this composition, containing 45% chocolate liquor, with no cocoa, may be safely used, if a long storage period, not exceeding one month, is not contemplated.

Other compositions may be similarly prepared from hard butters containing more or less herring flakes depending on the location, the season and the temperature at which the food products must be stored. Similarly the hard butters from marine oils in accordance with the instant invention may be incorporated, together with chocolate liquor, into light compound coatings, where the percentage of cocoa is ordinarily in the range of 8 to 9%, skim milk powder in the range between 6 and 8%, and sugar between 52 and 54%, as indicated in Table 4. The partial or total replacement of cocoa with chocolate liquor is just as satisfactory, in accordance with this instant invention, in the case of light compound coatings as with dark compound coatings.

The hard butters, prepared from marine oils may also be satisfactorily used in white coatings, in combination with milk solids, fine sugar, vanillin and an emulsifier, usually lecithin.

Different procedures may be used for the preparation of the compound coating compositions containing chocolate liquor. According to the preferred procedure, all the ingredients, the hard butter, cocoa, chocolate liquor, milk solid powder, sugar, lecithin, salt and flavoring agent, usually vanillin, are measured and combined, with the exception of about one-half of lecithin and a small portion of the hard butter, about 2 to 4%. After blending, the temperature of the mix is 120° to 145°F. The blend is refined to reduce the particle size to a

range between 25 and 40 microns. The coating is placed in storage tanks, at temperature of 135° to 145°F. for about 24 hours, during which time it is stirred in order to lower and stabilize the viscosity. The residual portions of 2 to 4% hard butter and lecithin are then added for the purpose of further lowering the viscosity. The coating is then tempered and molded into blocks, or kept in the melted state. It may be shipped either in the solid or melted form.

These coating compositions may be used for a variety of products such as icing of cakes and cookies, coatings of ice cream bars and candies. The finished food products are superior to other conventional preparations, because of their richer flavor and superior gloss.

WHAT WE CLAIM IS:—

1. Hard butter compositions which are the product of interesterification of a blend consisting of between 10 and 50% of an all-hydrogenated fat, prepared from an oil which is rich in oleic acid which contains palmitic acid and is free from lauric acid, said oil being an animal, vegetable or marine oil; and between 90 and 50% of a lauric acid-containing oil which is half-hydrogenated palm kernel oil, coconut oil or babassu oil.

2. A composition according to claim 1, in which the all-hydrogenated fat is all hydrogenated lard, tallow, peanut, cottonseed, soybean, palm, sesame oil, sunflower, safflower, corn, menhaden, or a combination thereof, and the iodine value after hydrogenation is not higher than 3.

3. A hard butter composition which is the product of interesterification of a blend consisting of between 10 and 50% of an all-hydrogenated marine oil, which is a member selected from the group consisting of herring oil, whale oil, menhaden oil, sardine oil and mixtures thereof, and between 90 and 50% of a lauric acid-containing oil, which is a member selected from the group consisting of half-hydrogenated palm kernel oil, coconut oil and babassu oil.

4. A hard butter composition according to claim 3, which comprises the product of interesterification of a blend consisting of 30% of all-hydrogenated herring oil and 70% of half-hydrogenated palm kernel oil, coconut oil or a mixture thereof.

5. A hard butter composition according to claim 3 or 4, which is the product of interesterification of a blend consisting of 30% herring flakes and 70% of partially hydrogenated palm kernel oil of refractive index between 25.5 and 25.7 at 60°C.

6. A chocolate coating composition which comprises sugar, an emulsifier, milk solid, a hard butter according to claim 3, and chocolate liquor in amount up to 45% of the finished composition, said composition also containing cocoa when the chocolate liquor is present in amount less than 45% of the finished composition.

7. A chocolate coating composition which comprises a blend of a hard butter according to claim 4, in amount between 10 and 30% milk solid in amount between 5 and 8%, an emulsifier in amount between 0.3 and 0.4% and sugar in amount between 42 and 54%, and chocolate liquor in amount up to 45% of the finished composition, said composition also containing from 8 to 18% cocoa when the chocolate liquor content is less than 45%.

8. A chocolate coating composition which comprises between 15 and 18% of cocoa, 5% of chocolate liquor, between 38 and 40% of sugar, between 5 and 6% of milk solid, vanillin in amount up to 0.1%, salt in amount between 0.1 and 0.2%, lecithin in amount between 0.3 and 0.4%, and 30% of a hard butter according to claim 5.

9. A chocolate coating composition comprising 14% of cocoa, 10% of chocolate liquor, between 38 and 40% of sugar, between 5 and 6% of milk solids, between 0.3 and 0.4% of lecithin, vanillin in amount up to 0.1%, salt in amount of 0.1 to 0.2%, and 29% of a hard butter according to claim 5.

10. A chocolate coating composition comprising 11% of cocoa, 15% of chocolate liquor, between 37 and 38% of sugar, between 0.08 and 0.1% of vanillin, between 0.1 and 0.2% of salt, between 0.3 and 0.4 of lecithin, and 28% of a hard butter according to claim 5.

11. A chocolate coating composition comprising 8% of cocoa, 20% of chocolate liquor, between 37 and 38% of sugar, between 5 and 6% of milk solids, between 0.08 and 0.1% of vanillin, between 0.1 and 0.2% of salt, between 0.3 and 0.4% of lecithin, and 25% of a hard butter according to claim 5.

12. A chocolate coating composition comprising 7% of cocoa, 25% of chocolate liquor, between 38 and 40% of sugar, between 5 and 6% of milk solids, between 0.3 and 0.4% of lecithin, vanillin in amount up to 0.1%, between 0.1 and 0.2% of salt, and 20% of a hard butter according to claim 5.

13. A chocolate coating composition comprising 35% of chocolate liquor, between 1 and 2% of cocoa, between 37 and 38% of sugar, between 5 and 6% of milk solid, between 0.1 and 0.2% of salt, between 0.3 and 0.4% of lecithin, vanillin in amount up to 0.1%, and 14% of a hard butter according to claim 5.

14. A chocolate coating composition comprising 45% of chocolate liquor, 38% of sugar, 5.5% of milk solids, vanillin in amount up to 0.1%, salt between 0.1 and 0.2%, lecithin in amount between 0.3 and 0.4%, and 10% of a hard butter according to claim 5.

15. A method of preparing a hard butter composition which comprises the steps of:

a) hydrogenating a marine oil which is a

member selected from the group consisting of herring oil, menhaden oil, whale oil, sardine oil, and mixtures thereof, until the iodine value is not higher than 3;

b) hydrogenating to a refractive index between 25 and 25.8 at 60°C., a lauric acid-containing oil, which is a member selected from the group consisting of coconut oil, palm kernel oil and babassu oil and mixtures thereof;

c) blending between 10 and 50% of the product from step a) with 90 and 50% of the product from step b);

d) subjecting said blend to interesterification, and

e) purifying said interesterified product from the reaction mixture until said hard butter is free from odors.

16. A hard butter composition substantially as hereinbefore described with reference to the Examples.

17. A chocolate coating composition substantially as hereinbefore described with reference to the Examples.

18. A method of preparing a hard butter composition substantially as hereinbefore described with reference to the Examples.

STEVENS, LANGNER, PARRY & ROLLINSON,
Chartered Patent Agents,
Agents for the Applicants.

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1968.
Published by the Patent Office, 25 Southampton Buildings, London, W.C.2, from which copies may be obtained.